Characterization of Graphene Conductance Using a Microwave Cavity

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***Abstract*— Surface conductance of graphene films is investigated in a non-contact microwave cavity operating at 7.4543 GHz. This cavity technique characterizes specimens with high accuracy, without disruption of morphological integrity and without the processing required for definition and application of electrical contacts. The thickness of the conducting 2D material does not need to be explicitly known. Measurement results are illustrated for epitaxial mono-layer graphene formed on 4H-SiC(0001) wafers by annealing the substrate via high fidelity Si sublimation. We show that the resonant microwave cavity is sensitive to the surface conductance of atomically thin nano-carbon films. The method is applied to characterize diffusion of water through a thin film moisture barrier coated over epitaxial monolayer graphene. The monolayer graphene is lightly *n*-type doped and therefore the resulting surface resistance value becomes sensitive to complexation with *p*-type molecular dopants such as water in moisturized air. Our results suggest that coating graphene surface with 100 nm thick Parylene-C film serves as effective moisture barrier. The observed change in conductance of Parylene-C specimens after environmental stress is within 6 % of the pre-test value and would satisfy the typical reliability requirements.**

Keywords—microwave cavity, surface conductance, epitaxial graphene, moisture barrier, molecular doping.

I. INTRODUCTION

Recent years have witnessed many breakthroughs in research as well as a significant investment in the advancement of the mass production of graphene materials. The market of graphene applications is essentially driven by progress in the production of graphene with properties appropriate for the specific application. There are several methods being used and developed to prepare graphene-like materials of various dimensions, morphology and number of layers. However, they are being offered with unreferenced quality, defect density and type, as these parameters affect these material's fundamental properties and behaviors. In this context, a graphene reference material for which the surface conductance can be related to number of layers, mobility and fundamental physical constants can be a breakthrough that may change the face of the industry. Here we characterize conductance of a mono layer epitaxial graphene on silicon carbide, where mobility and density of charge carriers are traceable through Hall resistance measurements. Surface conductance is determined at room temperature by a non-contact microwave cavity measurement. Surface conductance is determined at room temperature by a non-contact microwave cavity measurement. The method is nondestructive, experimentally simple and it does not require any electrical contacts that would otherwise obscure complexation with molecular dopants. The monolayer epitaxial graphene in conjunction with the non-contact microwave cavity method has the potential to be used as a 2D surface conductance/resistance reference material that would enable the industry to assess the quality and the corresponding electronic properties of their product. We investigate affinity of graphene to molecular complexation with environmental water under environmental stress conditions.

II. EXPERIMENTAL

A. Preparation of epitaxial graphene

Mono-layer epitaxial graphene on the Si-terminated face (SiC/G) was grown on high purity 4H-SiC(0001) 330 μm thick wafers. The substrates were annealed at 1900°C in Argon at (101-105) kPa using a controlled Si sublimation process, which stops at one mono-layer on Si-terminated face [1]. The wafers were then diced to obtain specimen size of 7.8 mm × 3.7 mm. After removing the graphene material on the C-terminated face, several SiC/G samples were tested directly in the microwave cavity on the native substrate. Hall resistance (ρ_{xy}), longitudinal resistance (ρ_{xx}), carrier concentration (n) and Hall mobility (μ) were measured on the corresponding samples at temperatures from 1.5 K to 30 K, using a Hall-bar device having a channel size 100 μm × 600 μm. At temperature of 298 K the Hall mobility of SiC/G is about 3200 $cm^2V^{-1}s^{-1}$, and the measured σ_G corresponds to the density of charge carriers, n, of about 1.7×10^{11} cm^{-2}. Due to interaction of the monolayer graphene with impurity scattering charge carriers at the graphene SiC substrate interface, the monolayer graphene is slightly *n*-type doped and therefore the resulting surface resistance value becomes sensitive to complexation with *p*-type molecular dopants such as water in moisturized air [2-4]. We applied Parylene-C thin film conformal coating as a protective barrier. Parylene-C

(poly-chloroxylylene) was deposited on the surface of selected SiC/G specimens in vacuum by pyrolysis at 600 ºC, followed by polymerization at 25 ºC, to obtain coatings about 100 nm thick [3]. Permeability of Parylene coatings was evaluated by exposing specimens to humid air and measuring a decrease of SiC/G surface conductance in correlation with the number of charge carriers immobilized by complexation with water molecules.

B. *Measurement of surface conductance by the non contact cavity perturbation method*

In our earlier work [5, 6] we showed that for a small conducting specimen inside a rectangular cavity operating in the TE_{10n} mode, solution of the imaginary part of cavity perturbation equation can be expressed by (1):

$$y'' = \varepsilon'' 4x - 2b'' \tag{1}$$

where, $x = V_s/V_0$, $y'' = 1/Q_s - 1/Q_0$, V_0 is the volume of the cavity, V_s is the volume of the specimen ($V_0 >> V_s$). Q_0 is the quality factor of the empty cavity and Q_s is the quality factor of the cavity loaded with the specimen. In the case of conducting materials with high mobility of delocalized charge carriers, such as graphene, the energy loss resulting from dipolar polarization and polarization of bound charges can be neglected, and the dielectric loss factor, ε''_r, is fundamentally equivalent to conductivity. This relation can be expressed in terms of surface conductance [5], which after substituting into (1) leads to (2):

$$\frac{1}{Q_x} - \frac{1}{Q_0} = \sigma_G \frac{2wh_x}{\pi \varepsilon_0 f_x V_0} c_\omega \tag{2}$$

where, σ_G is the surface conductance of graphene, ε_0 is the permittivity of free space, wh_x is the area of the graphene layer in the cavity, Q_x is the quality factor of cavity partially loaded with the graphene at wh_x, $c_\omega = (f_x/f_0)^2$ accounts for frequency correction due to substrate polarization, f_x is the resonant frequency of sample-loaded cavity and Q_0, and V_0 are the same as defined in (1). The quality factor is obtained from the resonant peak according to the conventional half power bandwidth formula as $Q_x = f_x/\Delta f_x$. Equation (2), from which we determine σ_G, does not depend explicitly on the thickness of the graphene layer, but on its area, wh_x, which can be determined with much higher accuracy than t_G. In the range of h_x where b'' is constant, (2) reduces to a linear equation with slope of σ_G. In the case when the surface conductance is comparable with that of the substrate and cannot be neglected, the conductance of the graphene layer can be extracted using a parallel admittance model of combined conductance described in Ref. [6]. Our cavity test fixture design shown in Fig. 1 employs a WR 90 waveguide (a=10.16 mm, b=22.86 mm, l_z = 127.0 mm) operating in the microwave frequency range of 6.7 GHz to 13 GHz. The fixture is connected to a network analyzer (Agilent N5225A) with semi-rigid coaxial cables and coaxial to WR 90 coupling adapters. The walls of the cavity are implemented via WR 90 couplers, which are near cross-polarized in respect to the waveguide polarization to achieve optimal power loading into cavity while maximizing the quality factor. The specimen is inserted into the cavity through a slot machined in the center of the cavity, where the electric field, $\boldsymbol{E}_x$, attains a maximum value. The specimen insertion (h_x), and the corresponding area of the material in the cavity (wh_x) are controlled by a stage.

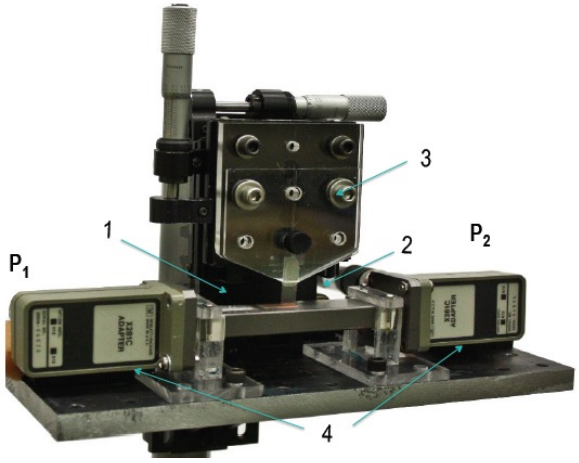

Fig. 1. Microwave cavity test fixture. (1) WR90 waveguide, (2) Specimen, (30) Specimen holder, (4) Coax to WR90 cross-polarized couplers, ports to vector network analyzer ($P_1$and P_2).

During measurements, the specimen is partially inserted in steps, while the scattering parameter, $\mathbf{S}_{21}$, is recorded. The implemented non-contact microwave cavity technique is applicable to materials having surface conductance from 10^{-6} S to 10 S. The surface conductance can be determined with the combined relative uncertainty of 1.5 %.

RESULTS AND DISCUSSION

Fig. 2 exemplifies the scattering parameter |magnitude, $|\mathbf{S}_{21}|$, of the TE_{103} mode measured for the epitaxial graphene as a function of the specimen insertion into cavity. The height of the resonant peaks of the SiC/G decrease and widen considerably with increasing specimen insertion due to conductance of the graphene layer. In comparison, the height and width of the resonant peaks of SiC (not shown) remains relatively unchanged with increasing specimen insertion, indicating low conductivity. From (2), σ_s of SiC substrate is in the range of 10^{-7} S. When aligned, the position of resonant peaks of SiC/G and the SiC substrate overlaps. Thus, the frequency shift of the resonant peaks in Fig 2 to lower frequencies is primarily due to the dielectric permittivity of the SiC substrate for which we find the dielectric constant, ε'_r of SiC to be 9.4 at the operational frequency of 7.435 GHz. Therefore, the frequency shift due to graphene is zero, that is, the real part of the relative permittivity of our epitaxial mono-layer graphene $\varepsilon'_r \approx 1.0$, which agrees well with the dielectric permittivity of truly 2D materials. This indicates that our SiC/G is of very high quality 2D monolayer graphene, practically free from polarizable defects. Evidently, we observe a coherent-like

response from a 2D lattice composed of C-2p_z conjugated electronic system with high charge carriers mobility.

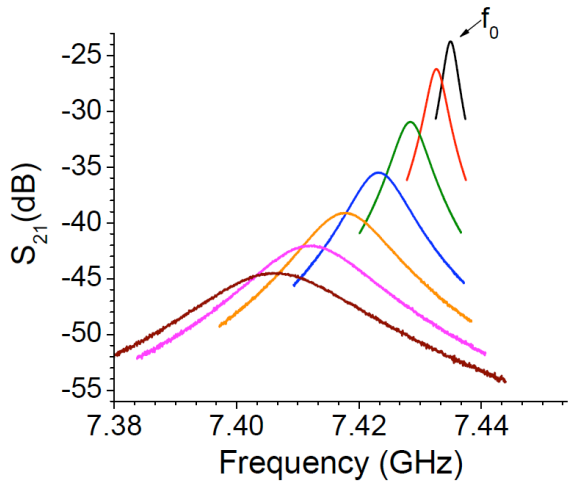

Fig. 2 Scattering parameter $|\mathbf{S}_{21}|$ of the resonant peak TE_{103} measured for SiC/G specimen. The peak position moves from f_0 to lower frequencies with increasing specimen insertion area (wh_x) due to dielectric constant od SiC. The peak decreases and widens with increasing insertion due to conductance of the graphene layer; f_0 = 7.434935 GHz.

In contrast, in the case of graphene materials with multi-layer graphene patches, voids, 3D or amorphous carbon impurities, polarization at the grain boundaries gives rise to di-polar polarization causing an additional shift in resonant frequency, beyond that corresponding to polarization from the dielectric substrate.

Fig. 3 shows graphical representation of (2), with experimental Q_x and h_x data for unprotected SiC/G at several RH conditions. These are compared with specimens coated with 100 nm thick barrier layer of Parylene-C. The solid lines are linear fits to (2) through the data points. In the presented notation, the surface conductance, σ_G, is obtained directly from the slope of the linear portion of the plots. When exposed to environmental moisture, surface conductance of freshly prepared SiC/G drops to certain saturated level. The effect of molecular complexation of water on SiC/G conductance is entirely reversible. After heating the exposed specimen at 130 ºC for few hours under Argon-moisture-free atmosphere, conductance increases back to its initial value, $\sigma_G = 8.7507\times10^{-5}$ S (see Fig. 3 plot 1).

From the slope of plots 2-4 in Fig 3 we find that at the relative humidity RH=20 % the 24 h saturated value of σ_G decreases to 5.593×10^{-5} S, at RH=30 % σ_G decreases to 5.264×10^{-5} S and at RH of 60 % the 24 h saturated value of σ_G approaches 4.5525×10^{-5} S. Based on our earlier investigations we may assume that within our experimental conditions the charge carriers mobility, μ_0 = 3200 $cm^2V^{-1}s^{-1}$, remains negligibly affected by the complexation process [7]. Therefore, density of charge carriers is directly relatet to conductance, $n_i = \sigma_{G\text{-}0}/e\,\mu_0$, and it decreases from its initial value n_1= 17.09 $\times10^{10}$ cm^{-2} to n_2=10.924 $\times10^{10}$ cm^{-2} at RH 20%, n_3=10.028 $\times10^{10}$ cm^{-2} at RH 30% and to n_4=8.891 $\times10^{10}$ cm^{-2} at RH 60%. In comparison, conductance of the specimens coated with Parylene protective layer remains essentially unchanged when exposed to ambient humidity-temperature (50% RH 20 ºC) for several weeks. Yet, after exposure to an accelerated environmental stress we noticed a decrease in surface conductance. Plots 5 and 6 in Fig. 3 show measurement results obtained for Parylene coated specimens that were exposed to accelerated environmental stress at 60 ºC, 85 % RH for 336 h (two weeks).

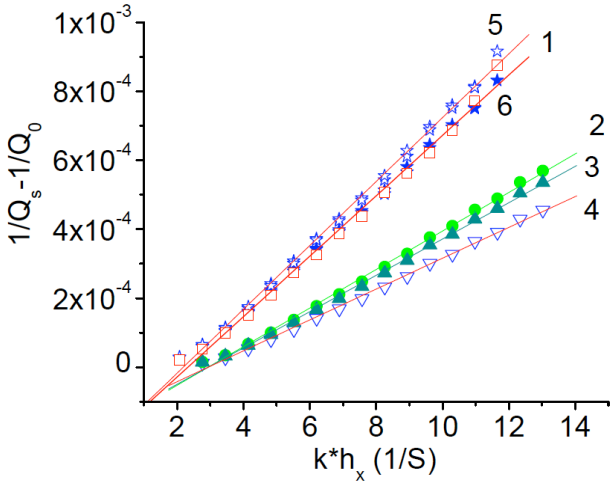

Fig.3. Plots of $(1/Q_s\text{-}1/Q_0)$ vs normalized specimen area (kh_x) for monolayer epitaxial graphene: (1-open squares) after heating in argon, (2-filed circles) exposured RH 20%, (3-filed triangles) RH 30%, (4-open triangles) RH 60%, (5-open stars) coated with Parylene and (6-filled stars) Parylene coated after environmental stress. The solid lines are linear fits to (2) through the data points where the slope respresents conductance, σ_G.

The observed decrease in conductance from that of Argon conditioning level of 9.27×10^{-5} S (plot 5) to 8.7507×10^{-5} S after the stress (plot 6), is detectable by our non-contact measurement method. The corresponding change in the number of charge carriers $\Delta n \approx 1.01 \times10^{10}$. The observed change in conductance is relatively small, about 6% and would likely satisfy the typical reliability requirements for SiC/G as a conductance reference for other graphene materials

Assuming that complexation takes one electron per water molecules then about 1×10^{10} water molecules can permeate through 1 cm^2 area of 100 nm thick barrier over 336 h diffusion time. Transferring these numbers from the molecular nanoscale to technical system of units (kg, m, s), one can find that ($\Delta n/6.07 \times10^{23}$ mol) $\times18 \times10^{-3}$ kg/mol) $\approx 3 \times10^{-16}$ kg of water permeates over 1×10^{-4} m^2 area , distance 10^{-7} m in 1.21 $\times 10^6$ s. These results are significant and prove the usefulness of the presented non-contact measurement methodology to evaluate permeability of nano-size thin film coatings in general.

III. Summary

We characterized conductance of a mono layer epitaxial graphene on silicon carbide with mobility and density of charge carriers traceable through Hall resistance. Surface conductance is determined at room temperature through a non-contact resonant microwave cavity measurement, and since no additional processing is required, it preserves the integrity of the conductive graphene layer. Like other non-contact methods (i.e., ellipsometry and optical density) it allows characterization

with high speed and efficiency, compared to transport measurements where sample contacts must be defined and applied in multiple processing steps. By using 100 nm thick layer of Parylene-C conformal coating as a protective encapsulation layer, stability of graphene electrical properties is considerably improved. After exposure to accelerated stress at 60 ºC, 85 % RH for 336 h the observed change in surface conductance was less than 6 % of its pre-stress test value, which would satisfy the typical reliability requirements for consumer electronics. We believe that such epitaxial graphene can be used as 2D conductance/resistance reference material that would enable the industry to assess the quality and the corresponding electronic properties of their product, without ambiguity. The presented results can be applied for permeability characterization of nanoscale aqueous barriers. Our approach allows determining diffusion of water molecules through thin protective encapsulation layers coated on graphene surface with resolution unobtainable by conventional methods.

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DISCLAIMER

Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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